

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification⁴ : C08F 2/20	A1	(11) International Publication Number: WO 90/02763 (43) International Publication Date: 22 March 1990 (22.03.90)
(21) International Application Number: PCT/US89/03767 (22) International Filing Date: 31 August 1989 (31.08.89) (30) Priority data: 8821631.2 2 September 1988 (02.09.88) GB (71) Applicant (for all designated States except US): BIOSYN-R CORPORATION [US/US]; 108 Rex Avenue, Philadelphia, PA 19118 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): VINCENT, Brian [GB/GB]; 4 Oakwood Avenue, Henleaze, Bristol BS9 4NS (GB). OBEY, Timothy, M. [GB/GB]; 1 Village Road, Enfield, Middlesex EN1 2DV (GB). CAWDERY, Nicolas, S. [GB/GB]; Greencroft 2 Eghams Wood Road, Beaconsfield, Bucks HP9 1JP (GB). (74) Agents: PABST, Patrea, L. et al.; Kilpatrick & Cody, 100 Peachtree Street, Suite 3100, Atlanta, GA 30303 (US).		(81) Designated States: AT (European patent), BE (European patent), CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i>
(54) Title: DISPERSIONS OF ELECTRICALLY CONDUCTING POLYMERS (57) Abstract The present invention is a method of preparation of "bare" dispersions of electrically conducting polymers, and products thereof. In particular, the invention provides a method to prepare charge stabilized, colloidal dispersions of conducting polymer particles which do not contain significant quantities of sterically stabilizing polymers, and the products thereof. These particles have many advantages over the prior art since they can be used to make non-aqueous dispersions of electrically conductive particles, or incorporated into high surface area electrodes and chromatographic and electrophoretic materials.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MR	Mauritania
BE	Belgium	GA	Gabon	MW	Malawi
BF	Burkina Faso	GB	United Kingdom	NL	Netherlands
BG	Bulgaria	HU	Hungary	NO	Norway
BJ	Benin	IT	Italy	RO	Romania
BR	Brazil	JP	Japan	SD	Sudan
CA	Canada	KP	Democratic People's Republic of Korea	SE	Sweden
CF	Central African Republic	KR	Republic of Korea	SN	Senegal
CG	Congo	LI	Liechtenstein	SU	Soviet Union
CH	Switzerland	LK	Sri Lanka	TD	Chad
CM	Cameroon	LU	Luxembourg	TG	Togo
DE	Germany, Federal Republic of	MC	Monaco	US	United States of America
DK	Denmark				

DISPERSIONS OF ELECTRICALLY CONDUCTING POLYMERS

This application is in the field of polymer chemistry, and is in particular a method of forming dispersions of electrically conducting latex particles.

5

Background of the Invention

Colloidal particles having a high electrical conductivity have mainly been metal particles, perhaps the most famous being Faraday's gold sol preserved in The Royal Institution in London. However, many other
10 types of metal sols have now been produced, particularly for use in heterogeneous catalysis. During the last decade or so there has been rapidly growing interest in organic polymers which show high electrical conductivities comparable to the electrical
15 conductivities of metals.

The most studied conducting polymer system is polyacetylene. Although pristine polyacetylene is a semiconductor, MacDiarmid et al. (M. M. Maricq, J. S. Waugh, A. G. MacDiarmid, H. Shirakawa, and A. J.
20 Heeger, J. Amer. Chem. Soc. 100, 7729 (1978)) demonstrated that doping the bulk or surface polymerized material with a suitable oxidizing agent (e.g., I_2 , AsF_5 , $FeCl_3$) or reducing agent (e.g., Na, n-BuLi) can lead to very high conductivities, greater
25 than $1 \Omega^{-1} \text{ cm}^{-1}$. However, the possible exploitation of polyacetylene, prepared in this way, has been severely restricted, largely because of the intractability of the material and its sensitivity to atmospheric oxidation.

30 One potential way of overcoming these disadvantages is to start with colloidal polyacetylene. Edwards, Fisher and Vincent, in

-2-

Macromol. Chem. Rapid Commun. 4, 393 (1983), described the preparation of latex polyacetylene particles by a nonaqueous dispersion polymerization route. However, although the particles produced could
5 be doped, e.g., with I_2 , from either the vapor phase or the solution, the conductivities obtained for the pelletized material were not as high as those reported for bulk polymerized material.

Dispersion polymerization involves the
10 polymerization of a monomer dissolved in a liquid which is a solvent for the monomer and initiator but a nonsolvent for the polymer, where a dispersant is added to prevent gross flocculation of the polymer and to control particle size. The dispersant also
15 prevents aggregation of polymer particles caused by high salt content in the solvent. Water soluble dispersants are generally organic polymers such as gelatin, methyl cellulose, poly(vinyl alcohol) and alkali salts of poly(methacrylic acid). See
20 generally, G. Odian, Principles of Polymerization, (2nd Ed. 1981), K. E. J. Burrett, Dispersion Polymerization in Organic Media; Wiley, New York, 1975, incorporated herein by reference.

Bjorklund and Lundstrom prepared
25 polypyrrole/cellulose composites by an aqueous dispersion technique. The composites have a conductivity of $2 \text{ ohm}^{-1}\text{cm}^{-1}$, when measured in a dilute HCl solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, as reported by R. B. Bjorklund and I. Lundstrom, J. Electron. Mater. 13,
30 211 (1984). Bjorkland and Liedberg later reported that the resulting polymeric composition had essentially no Fe^{+3} ion present while the Cl^- anion was neutralizing the charge on the polymer. The composite was used to prepare thin films displaying a

-3-

maximum conductivity of $0.2 \text{ ohm}^{-1} \text{ cm}^{-1}$, as described by R. Bjorkland and B. Liedberg, in "Electrically Conducting Composites of Collodial Polypyrrole and Methyl Cellulose", J. Chem. Soc. Chem. Commun., 1293
5 (1986).

The emeraldine salt form of polyaniline is prepared by adding aniline to an aqueous solution of $(\text{NH}_4)_2\text{S}_2\text{O}_8$. The polymer has a symmetric conjugated structure with extensive charge delocalization and a
10 high conductivity resulting from proton addition to the polymer. This is in contrast to partial oxidation of the polymer π system, as in the p-doping of other conducting polymers, W. Huang, B. Humphrey, and H. MacDiarmid, "Polyaniline, a Novel Conducting
15 Polymer", J. Chem. Soc. Farady Trans. 1, 82, 2385 (1986).

Myers reported in "Chemical Oxidative Polymerization as a Synthetic Route to Electrically Conducting Polypyrroles", J. Electr. Mater., 2 61
20 (1986), that various transition metal compounds, specifically Fe^{+3} and Co^{+2} complexes, function both as polymerization initiators and as dopants in converting pyrrole and substituted pyrroles into electrically conducting polymers. The conductivities of the
25 resulting polymers varied by a factor of 10^8 , from 10^{-6} to $10^2 \text{ ohm}^{-1}\text{cm}^{-1}$, depending on the choice of oxidant and overall reaction conditions. Product yields and rates of reaction were also dependent on the oxidant used as the initiator.

30 In "Dispersions of Electrically Conducting Polypyrrole Particles in Aqueous Media", J. Chem. Soc. Chem. Commun. 288 (1987) and "Aqueous Dispersions of Electrically Conducting Monodisperse Polypyrrole Particles", J. of Collodial and Interface Science

-4-

118(2), 410 (1987), Armes and Vincent reported the preparation of conducting polypyrrole particles, in the size range of 50-250 nm diameter, by dispersion polymerization using FeCl_3 as initiator-dopant and poly(vinyl pyrrolidone) (PVP) and poly(vinyl alcohol-co-acetate) (PVA, 88 or 96% poly(vinyl alcohol) as dispersant or stabilizer. They reported that PVA led to more monodisperse particles and required a lower ratio of stabilizer to monomer for successful particle formation than PVP. The method of preparation of the conducting particles reported by Armes and Vincent involved the addition of pyrrole to an aqueous solution of anhydrous FeCl_3 and the dispersant. The characteristic brown-black color of doped polypyrrole developed within a few minutes. The latex particles formed by this procedure had conductivities in the range of 10^{-1} to $10 \Omega^{-1}\text{cm}^{-1}$, as measured by both the standard van der Pauw method (L. J. van der Pauw, Philips Res. Rep. 13(1), (1958)) and the four-point probe (F. M. Smits, Bell Syst. Tech. J. 711 (1958)).

Armes and Vincent found a decreasing trend in mean particle size with increasing adsorption the dispersant. The small apparent decrease in size of the polypyrrole particles with increasing PVA concentration is related to the precursor particle stage in the polymerization. There is competition between the rate of aggregation of these very small precursor particles and the rate of adsorption of the stabilizing polymer. Effective stabilization is not achieved below a certain minimum PVA concentration.

Another problem that results from the adsorption of polymeric dispersant by the growing conducting polymer is the decrease in conductivity with increasing mass ratio of dispersant to monomer in the

-5-

particle. This is a direct effect of incorporation of nonconducting dispersant into the conducting pellet. The dispersant cannot be eliminated from the method of preparation of the latex particles, however, because
5 it is needed in the dispersion polymerization reaction to prevent aggregation of the polymer particles as a result of high salt content.

Therefore, it is an object of the present invention to provide a method of preparing dispersions
10 of polymeric conducting particles that have minimal or no dispersant adsorbed to the particles.

It is a further object of this invention to provide a method of preparation of organic conducting particles which results in particles with high
15 conductivities.

It is another object of the present invention to prepare polymeric conducting particles which may be dispersed in a solvent without a stabilizing polymeric coating.

20 Summary of the Invention

The present invention is a method of preparation of "bare" dispersions of electrically conducting polymers, and products thereof. In particular, the invention provides a method to prepare charge
25 stabilized, colloidal dispersions of electrically conducting polymer particles which do not contain significant quantities of water soluble sterically stabilizing polymers, and the product thereof.

According to the present invention, charge-
30 stabilized "bare" conducting polymeric particulate dispersions are produced by polymerizing an electrically conducting polymer in an aqueous

-6-

solution containing a water soluble stabilizing/dispersant polymer (referred to hereafter as stabilizing polymer), then stripping the particles of the stabilizing polymer. For example, a sterically
5 stabilized conducting polymeric latex can be polymerized from an aqueous solution of monomer, initiator and stabilizing polymer, followed by removal of the stabilizing polymer by repeated washing with a solvent for the stabilizing polymer, chemical or
10 biological degradation of the stabilizing polymer sheath, or by manipulation of the solution pH, promoting repulsion between the conducting polymer and the stabilizing polymer.

The bare particles may be freeze dried or
15 redispersed in solution after stripping the conducting particles of their dispersant-stabilizing polymer sheath. To disperse the charge-stabilized particles in solvents of low dielectric constant or high ionic strength, a dispersant-stabilizing polymer is added to
20 the solvent. One advantage of the present invention is that the bare particles can be resuspended in a non-aqueous solvent and coated with block or graft copolymers which are not soluble in aqueous solutions. The bare or recoated particles can also be
25 incorporated onto or within non-conducting polymeric particles or latices.

This method produces polymer particles having approximate diameters of 40 to 500 nm which have conductivities in the range of approximately one to
30 ten $\Omega^{-1} \text{ cm}^{-1}$.

The "bare" electrically conducting polymers obtained are useful for a variety of applications, including incorporation into electrically conducting composites, chromatographic materials, adsorbents,

high surface area electrodes, and electrophoresis materials.

Detailed Description of the Invention

5 The present invention is a method of producing "bare" electrically conducting polymeric particles and dispersions, and the products thereof. The method includes preparation of charge-stabilized colloidal dispersions which do not have adsorbed to them water particles of electrically conducting polymer
10 poly(ethylene oxide), stabilizing polymers such as poly(vinyl pyrrolidone), poly[vinyl alcohol-co-acetate], carboxymethacrylate (CMA), poly(methacrylic acid), and copolymers thereof. These particles can be dispersed in non-aqueous solutions and used in a variety of applications in addition to those which the polymer
15 coated particles can be used for. The particles have different properties, i.e., they can be readily aggregated by addition of electrolyte or adjustment of pH or used to absorb high surface area active agents or polymers from solution.

20 The method of the present invention to make charge-stabilized, or "bare", conducting polymeric particles is summarized as follows. An electrically conducting polymer is polymerized in an aqueous solution of a water soluble dispersant or stabilizing polymer, thereby forming
25 polymeric particles stabilized within a latex. The stabilizing polymers are defined as those which have properties similar to those of poly(ethylene oxide and poly[vinyl alcohol-co-acetate] with respect to their solvent miscibility and their interaction with the
30

-8-

electrically conducting polymers such as polyaniline and polypyrrole.

The stabilizing polymer is then removed from the particles. Several methods can be used. The three
5 preferred methods at this time are by repeated washing of the sterically stabilized conducting polymeric latex with a good solvent for the stabilizing polymer, by chemical or biological degradation of the polymeric sheath, and by manipulation of the solution
10 pH, to promote repulsion between the conducting polymer and the stabilizing polymer.

After stripping the conducting particles of their stabilizing polymeric sheath, the bare particles can be freeze dried or redispersed in the same or a
15 different solution. The particles can be directly suspended in solvents of high dielectric constant such as water or methanol or mixtures thereof. The conducting particles can be dispersed in solvents of low dielectric constant or high ionic strength if a
20 dispersant-stabilizing polymer is added to the solvent. Since the bare particles can be dispersed in non-polar solvents, non-water soluble stabilizing polymers can be added as the dispersants. For example, polymers which can be used in hydrocarbons
25 include polyacrylate with polyhydroxyteric acid, polylaurylmethacrylate, and polytertiarybutylstyrene. Bare particles can be dispersed in a solvent to a concentration of between approximately 50 to 100 g/l. Coated particles can be dispersed in a solvent to a
30 concentration of approximately 400 g/l.

This method produces conducting polymers particles which have conductivities in the range of approximately one to ten $\Omega^{-1} \text{ cm}^{-1}$.

-9-

Electrically conductive polymers which may be used according to the present invention include any polymer that conducts electricity, which can be dispersion polymerized and maintains its integrity
5 when the dispersant-sheath is removed. Examples of semiconducting organic polymers which can be used to make the polymeric particles of the present invention include polypyrrole (PPy), polyacetylene, polyaniline, polythiophene, poly(p-phenylene) and substituted
10 polymers thereof.

The monomers corresponding to these polymers are added to the solution in a concentration range of 0.5% to 5%, preferably 1%, by volume.

Initiators which can be used in the present
15 invention include Lewis acids such as ferric chloride (FeCl_3), ferric bromide (FeBr_3), $\text{Fe}(\text{NO}_3)_3$, $\text{K}_3\text{Fe}(\text{CN})_6$, CuCl_2 , CuBr_2 , $\text{Cu}(\text{NO}_3)_2$, AlCl_3 , BF_3 , SnCl_4 , ZnCl_2 , TiCl_4 , or PCl_5 , organometallic derivatives such as RAlCl_2 , R_2AlCl , R_3Al (where R is an organic ion),
20 oxyhalides such as POCl_3 , CrO_2Cl , SOCl_2 , VOCl_2 , acetyl perchlorate, and oxidizers such as potassium persulphate ($\text{K}_2\text{S}_2\text{O}_8$) and ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$). The selection of the initiator can be used to vary the particle size, which generally ranges
25 from approximately 40 nm to 500 nm in diameter. For example, smaller particles are produced when $\text{K}_2\text{S}_2\text{O}_8$ is employed as the initiator than when $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is used. The initiator is present in the solution in a range of between approximately 1% to 20% by mass,
30 depending on the particular initiator and monomer being used.

Oxidation of the conducting polymers within the particle by the initiator during polymerization leads

-10-

to an increase in the conductivity of the particles, i.e., intrinsic doping occurs.

Polymers suitable as dispersant-stabilizers in the present invention include poly(ethylene oxide) (PEO) (MW > 10^5), poly[vinyl alcohol-co-acetate], poly(vinyl pyrrolidone) (PVP), carboxymethylcellulose, carboxymethacrylate (CMA), poly(methacrylic acid), and copolymers thereof. Other polymers which can be utilized are known to those skilled in the art.

The stabilizing polymers are added to the solution in a concentration ranging from 0.3% to 3% by mass, preferably 1%.

The choice of stabilizing polymers can be used to modify the particle size. For example, the average diameter (\bar{d}) of the particles made using PEO as the stabilizer is significantly greater than when either PVP or PVA is employed. One may use this fact to manipulate the preparatory conditions to obtain a particle of desired size. Polypyrrole particles made using PVP or PVA have diameters typically in the range 70-150 nm. Particles made using PEO have larger diameters: $d = 445 \pm 45$ nm (PEO MW 3×10^5), $d = 350 \pm 40$ nm (PEO MW 4×10^6). These data reflect the much weaker adsorption affinity of PEO on PPy surfaces. With PVP or PVA, H-bonding between the N-H of the pyrrole moieties in the particle surface and the C=O of the pyrrolidone or acetate moieties of the stabilizer chains may play a role in determining particle size. Any similar interaction between the pyrrole N-H groups and the ether oxygen in the PEO chains is expected to be much weaker.

The "effective equilibrium adsorption isotherm" for the preparation of sterically-stabilized

-11-

conducting polymers may be prepared by plotting the mass ratio of stabilizer to monomer versus the equilibrium concentration of the stabilizing polymer in the solution used to prepare the dispersion. A
5 decrease in concentration of the dispersant stabilizer in the solution corresponds to an adsorption of the dispersant into the polymer particles. The isotherm curve rises to a certain height at which point the slope of the curve changes. This "knee" represents
10 the optimum stabilizing polymer to monomer mass ratio.

Composites of the bare electrically conducting polymeric particles are prepared by suspending the particles in a solution of monomer and stabilizing polymer and polymerizing. The particles can be bound
15 to the surface of non-conducting polymeric supports or larger oxide or carbon particles using methods known to those skilled in the art. Similarly, the particles can be adsorbed onto non-conducting latices or particles using methods and materials known to those
20 skilled in the art. These materials are particularly useful in absorbents, high surface area electrodes, electrophoresis and chromatographic reagents, and in other separation technologies.

The present invention is further described with
25 references to the following non-limiting examples.

Example 1: Modification of particle size by selection of stabilizing polymer.

Particles were prepared as summarized: 8.83 g of ferric chloride hexahydrate dissolved in 50 ml H₂O was
30 added to a stirred solution of X g of polymer in 50 ml H₂O. Freshly distilled pyrrole (1 ml) was added and stirring continued for 24 hrs at 25°C. The latex was then decanted into well-boiled "Visking" tubing and

-12-

dialyzed against water (the dialysate being changed every 12 hrs for a period of one week).

The particle size distributions were obtained from electron micrographs (Hitachi HA-11B electron microscope) with subsequent analysis using a Carl-Zeiss TGZ3 analyzer.

Conducting particles were prepared with diameters in the range of 80-440 nm. When PEO was used as the stabilizer, fairly large particles were obtained. Table 1 provides a representative list of particle sizes.

Table 1: Conducting Polymer Particle Sizes

<u>Code</u> <u>(nm)</u>	<u>x (g/100 cm)</u>	<u>max. diameter</u>
PPy/PVP44K	0.3	153 + 30
PPy/PVP700K	0.3	83 + 13
PPy/PVA95K	0.3	149 + 13
PPy/PEO300K	0.8	444 + 47
PPy/PEO4000K	0.8	356 + 42
PPy/CmCl	0.8	106 + 20
PPY/CMC2*	0.8	30 + 15

4.42 g $K_2S_2O_8$ used as initiator.

Example 2: Removal of stabilizing polymer from conducting polymer particles by washing with an appropriate solvent.

PEO was removed from PPy particles with repeated washing with a water/methanol mixture. Other water soluble polymers such as PVA and PVP can be removed by washing with other suitable solvents or mixtures thereof. Typically, bare PPy particles are produced from PPy/PEO composites after several, usually at least five, centrifugation/redispersals in water/methanol mixtures. Other suitable solvents can be determined by testing the solubility of the

-13-

dispersant-stabilizing polymer in the desired solvent system. The success of the removal step can be monitored spectrophotometrically with, for example, analysis of IR, NMR or UV, or, alternatively, by
5 performing standard wet qualitative chemical analyses. Elemental analysis can also be used to confirm that the dispersant-stabilizing polymer has been removed.

10 **Example 3: Demonstration of removal of the stabilizing polymer sheath from the electrically conducting polymer latex.**

One can determine whether the conducting polymer is "bare" and no longer sterically stabilized by addition of an electrolyte to the solution which leads to aggregation or flocculation if the system is
15 electrostatically stabilized, or by addition of a polymer to the solution that will adsorb to the "bare" particle but not the coated particle.

This is demonstrated as follows.

MgSO₄ (0.1 M) was added to each sample described
20 in Table 2 to obtain a final concentration of 0.05 M, and the extent of flocculation was checked after 24 hrs. The sterically stabilized particles were stable after 24 hours, while the charge-stabilized particules flocculated, suggesting that during washing of PEO-
25 stabilized PPy with water/methanol, stripping of the PEO sheath occurred.

-14-

Table 2: Flocculation of Polymers to demonstrate Stability

<u>Code</u>	<u>Stability after 24 hrs</u>
PPy/PVP44K	Stable
PPy/PVA95K	Stable
PPy/PEO300K	Stable
PPy/CMC1	Stable
PPy/PEO300K ¹	Flocc'd
PPy/PEO300K ²	Stable
PPy/PEO300K	Stable
PPy/PVP44K ⁴	Stable
PPy/PVA95K ¹	Stable
PPy/CMC1 ⁵	Flocc'd
PPy/CMC1 ⁶	Flocc'd
PPy/CMC ⁷	Stable
PPy/PEO300K ⁸	Stable

1. Redispersed in MeOH, final redispersal in H₂O.
2. As for 1 but NaPSS 780K added at pH 1.6.
3. As for 1 but final redispersal is 1,4-dioxan + PEO300K.
4. Redispersed in pyridine, final redispersal in H₂O.
5. Enzyme treated.
6. HCl treated 5 mol dm⁻³ - pure latex unstable after 24 hrs.
7. HCl treated 1 mol dm⁻³.
8. Acetic acid/HBr-treated.

Table 3 demonstrates the mass ratio of adsorbed NaPSS 780K per meter² polypyrrole particle surface. NaPSS is a negatively charged polyelectrolyte which is adsorbed onto a "bare" poly(pyrrole) surface which

-15-

carries a positive charge, but will not be adsorbed onto a polymer particle which has a steric-stabilizer sheath. For example, at pH 1.6, PPy/PEO particles that had been washed with water to remove PEO adsorbed approximately 3 mg/m² of NaPSS 780K. When the pH was raised to 11, the particles do not adsorb NaPSS, because the polymer is not protonated. Further, NaPSS adsorbed originally at pH 1.6 could be completely removed by raising the pH to 11. The amount of NaPSS 780K that may be adsorbed onto water/methanol-washed latex is far greater than on untreated latex, indicative of a loss of the stabilizing sheath.

Microanalytical results support this conclusion. For MeOH-washed samples, empirical formula very close to those of bulk-polymerized PPy are obtained, as shown in Table 4.

Table 3: Removal of Stabilizing Polymer from Conducting Polymer Particle Surface.

Code ⁵	r ⁴ (mg/m ⁻²)
PPy/PEO300K ¹	0.23
PPy/PEO300K ²	6.50
PPy/CMC1 ¹	1.00
PPy/CMC1 ³	5.25

1. Particles with dispersant-stabilizer sheath.
2. Redispersed in MeOH, final redispersal in H₂O.
3. Enzyme treated.
4. Mass ratio of adsorbed NaPSS 780K per meter² particle surface.
5. All solutions were acidified to pH 1.6 and equilibrated for 24 hrs.

-16-

Table 4: Formula Analysis of Bare Polymer Particles
Code⁴

PPy/PEO300K ¹	C _{4.61} H _{3.72} N ₁ Cl _{0.18}
PPV/PEO300K ²	C _{4.05} H _{3.2} N ₁ Cl _{0.17}
PPy/CMC1 ¹	C _{5.55} H _{5.34} N ₁ Cl _{0.18}
PPy/CMC1 ³	C _{5.01} H _{4.44} N ₁ Cl _{0.1}

1. Particles with dispersant-stabilizer sheath.
2. Redispersed in MeOH, final redispersal in H₂O.
3. Enzyme treated.
4. Analysis done on Perkin-Elmer 240 elemental analyzer.

Example 4: Redisperison of bare conducting polymer particles.

PPy/PEO 300K, PPy/PVA 95K and PPY/PVP 44K were spun down using an MSE 'Hi-Spin 18' centrifuge at
 5 15000 r.p.m. for 30 mins and redispersed in methanol (PPy/PEO 300K, PPy/PVA95K) or pyridine (PPy/PVP44K) using mechanical agitation and ultrasonics. Particles were redispersed six times, then the latices were redispersed in water. PPy/PEO 300K can also be
 10 dispersed in organic solvents (e.g. 1,4-dioxan) if dissolved polymer is present.

The results demonstrate that bare PPy latex particles in water (relative permittivity 80) can be redispersed in methanol (relative permittivity 33)
 15 using several centrifugation/redispersion cycles. However, the PPy particles cannot be redispersed in pure solvents of low relative permittivity e.g.

-17-

dioxane, unless redispersed from methanol into dioxan containing dissolved, dry high mw PEO.

Example 5: Removal of stabilizing polymer by chemical or biological degradation.

- 5 A second method of removing the adsorbed dispersant-stabilizer sheath is by chemical or biological degradation of the sheath. For example, ether linkages can be cleaved by suitable acids such as an acetic acid/HBr mixture, HI, HBr, and HCl.
- 10 Glucoside linkages can be cleaved by mineral acids. Enzymes known to cleave certain linkages in the stabilizing polymer can also be employed to remove the dispersant-stabilizer sheath. For example, cellulase is useful to remove carboxymethylcellulose from the
- 15 conducting polymer. For example, an ether linkage can be cleaved with an acetic acid/HBr mixture. PPy/PEO 300K was treated with a 50/50 mixture of acetic acid/HBr at 60°C for 24 hrs. Similarly glucoside links may be
- 20 cleared by the action of mineral acids, using the method described in "Introduction to Carbohydrate Chemistry", R. D. Guthrie, Clarendon Press (1979), or with cellulases, as described in "Hydrolysis of Cellulose: Mechanisms of Enzymatic and Acid
- 25 Hydrolysis" (R. R. Brown, Jr., L. and Juresek, wdx.) Adv. Chem. Ser. 101 (1980). PPy/CMC1 was treated with cellulose trichoviride at 37°C and pH 4.2 for 24 hrs, and HCl solutions of varying concentration (10^{-2} - 5 mol dm⁻³).
- 30 Acid hydrolysis of CMC stabilized PPy is not the preferred method for preparing electrostatistically-stabilized PPy, since very harsh conditions are needed to promote extensive degradation of the stabilizing sheath. At lower concentrations of acid, little of

-18-

the coating is degraded. Enzyme hydrolysis produces particles that behave as if they are uncoated. If enzyme is adsorbed at the particle surface, it may be denatured using base.

5 **Example 6: Removal of polymer using pH manipulation.**

A third method of producing a bare latex conducting polymer particle is by manipulation of the pH of the solution of the coated polymer particle. For example, at low pH poly(pyrrole) has a positive
10 charge and at high pH it has a negative charge. It is possible to desorb carboxymethylcellulose from the surface of the poly(pyrrole) by raising the pH of the system to promote repulsion between the polymer chain and the dispersant-stabilizer. Likewise, polyaniline
15 is positively charged at low pH and negatively charged at high pH. Suitable reagents to alter pH include HCl, acetic acid, HBr, and HI

Example 7: Measurement of electrophoretic mobility of bare polymers.

20 The electrophoretic mobility of both sterically and electrostatically-stabilized lattices was measured as a function of pH using a PenKem System 3000 instrument. The background of electrolyte level was maintained at 10^{-2} mol dm⁻³ (NaCl). The
25 electrophoretic mobility of the bare latex particles in aqueous 10^{-2} mol dm⁻³ KCl solution was measured as a function of pH. In general, bare particles have higher isoelectric points than do particles coated with stabilizing polymer.

30 **Example 8: Measurement of conductivity of bare polymeric particles.**

Particles were freeze dried to form pellets for conductivity measurements using a Research and Industrial Co. Model H301 pelletizing press at

-19-

pressures of 250 atm. The dc conductivities were obtained using the standard four point probe method, W. S. Huang, B. D. Humphrey, and A. G. MacDiarmid, J. Chem. Soc. Faraday Trans. 1 82, 2385 (1986).

- 5 Table 6 provides the results of the conductivity measurements.

Table 6: Conductivity of Polymers.

<u>Code</u>	<u>conductivity ($\Omega^{-1} \text{ cm}^{-1}$)</u>
PPy/PVP44K	2.7
PPy/PVA95K	0.8
PPy/PEO300K	0.8
PPy/CMC1	0.3
PPy/PEO300K*	0.01
PPy/PEO300K**	2.3
PPy/CMC1***	0.1

* redispersed in MeOH, final redispersal in H₂O

** redispersed in MeOH, final redispersal in 1,4 dioxane and PEO300K

*** enzyme treatment

The following reagents were used to obtain the materials and data discussed above.

- All water used was passed through a Permutit-250 ion-exchange column, then a Millipore Milli-Q water
 5 purification system and finally filtered using a Millipore 0.35 micron filter. Pyrrole (Aldrich Chemicals) was distilled under vacuum and stored under argon at 4°C in the absence of light. Ferric chloride (FeCl₃·6H₂O; BDH) potassium persulphate
 10 (K₂S₂O₈; BDH, 'AnalaR' grade) and cellulose trichoviride (Sigma) were all used as received.

Poly(vinyl pyrrolidone) (PVP), poly(ethylene oxide) (PEO), poly(acrylic acid) (PAA), and

-20-

carboxymethyl cellulose (CMC), were supplied by BDH. Poly(vinyl alcohol) (PVA) was supplied as 96% hydrolysed material (Aldrich Chemicals). Sodium poly(styrene sulphonate) (NaPSS) was supplied by
5 Polymer Laboratories Ltd. All were used as received.

Table 5: Polymer molecular weights.

<u>Code</u>	<u>Molecular weight, Mw</u>
PVP44K	44 000
PVP700K	700 000
PVA95K	95 000
PEO300K	300 000
PEO4000K	4 000 000
NaPSS780K	780 000
CMC	Not known*

* Viscosity of 1% solution at 20°C 1500 + 400 CP.

"Bare" conducting polymer particles prepared as described, are useful for a variety of applications. For example, such materials can be incorporated into conducting composites. Alternatively, the organic conducting materials may be used in selective extractive technologies. Since conducting polymers may vary in charge as a function of applied current, they can be used in electrochromatography, electrophoresis, or any like technique that separates a mixture of compounds on the basis of charge. Water stable conducting polymers have a broad range of biological applications, as in the separation of proteins and other biological materials. A further application of these "bare" latex organic conducting polymers is for electrically conducting paint. Such a coating can change the radar profile of aircraft.

-21-

Example 9: Preparation of Polypyrrole Particles in the size range of 40 to 100 nm.

Particles of less than 100 nm diameter were prepared by making two microemulsions of water droplets in toluene, one containing pyrrole monomer and the other containing an initiator, ammonium persulfate, dissolved in the aqueous phase. Within an hour of mixing the two microemulsions, a clear blue-black "solution" had formed; after 24 hours, a dark green supernatant containing a black precipitate of flocculated polypyrrole (PPY) particles formed. In order to produce stable particles during the 24 hour reaction period, aliquots of the reaction mixture were "flooded" periodically during the 24 hour period with a large excess of an aqueous solution of a polymeric stabilizer, polyvinylpyrrolidone of molecular weight 700,000. This procedure resulted in stable dispersions of the particles, which were then "cleaned" by several centrifugation/redispersion in water cycles. The average size of the PPY particles was then determined using photon correlation light-scattering. Particle size is a function of the time of reaction: the shorter the reaction time, the smaller the particle size. Particle size ranged from 50 nm at 100 minutes to 100 nm at 500 minutes, with sizes varying inbetween from approximately 50 to 60 nm at 125 to 150 minutes to 85 nm at 450 minutes.

Modifications and variations of the conducting polymer particles, and methods for their manufacture, will be apparent to those skilled in the art from the foregoing detailed description of the invention. Such modifications and variations are intended to come within the scope of the appended claims.

We claim:

-22-

1. A method to produce bare electrically organic conducting particles comprising:
polymerizing an electrically conductive polymer in the presence of an initiator and a stabilizing polymer to form particles of conducting polymer coated with stabilizing polymer, and removing the stabilizing polymer.
2. The method of claim 1 wherein the polymer is polymerized by aqueous dispersion.
3. The method of claim 1 wherein the stabilizing polymer is removed by washing the particle with a solvent for the stabilizing polymer but not the electrically conductive polymer.
4. The method of claim 1 wherein the stabilizing polymer is removed by chemical degradation.
5. The method of claim 1 wherein the stabilizing polymer is removed by biological degradation.
6. The method of claim 1 wherein the stabilizing polymer is removed by altering the solution pH.
7. The method of claim 1 wherein the polymer is polymerized from monomers selected from the group consisting of pyrrole, acetylene, aniline, thiophene, and p-phenylene.

-23-

8. The method of claim 1 wherein the initiator is selected from the group consisting of FeCl_3 , FeBr_3 , $\text{Fe}(\text{NO}_3)_3$, $\text{K}_3\text{Fe}(\text{CH})_6$, CuCl_2 , CuBr_2 , $\text{Cu}(\text{NO}_3)_2$, AlCl_3 , BF_3 , SnCl_4 , ZnCl_2 , TiCl_4 , PCl_5 , $\text{RAl}(\text{Cl})_2$, R_2AlCl , R_3Al (wherein R is an organic ion), POCl_3 , CrO_2Cl , SOCl_2 , VOCl_2 , $\text{CH}_3\text{CO}_2\text{ClO}_4$, $\text{K}_2\text{S}_2\text{O}_8$, and $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

9. The method of claim 1 wherein the stabilizing polymer is a polymer or copolymer of a monomer selected from the group consisting of ethylene oxide, vinyl acetate, vinyl pyrrolidine, carboxymethyl cellulose, vinyl alcohol, and methacrylic acid.

10. The method of claim 3 wherein the solvent is a mixture of water and methanol.

11. The method of claim 4 wherein the stabilizing polymer is removed by acid cleavage.

12. The method of claim 11 wherein the acid is selected from the group consisting of acetic acid/HCl, HBr, HCl, and HI.

13. The method of claim 5 wherein an enzyme is used to degrade the stabilizing polymer.

14. The method of claim 13 wherein the enzyme is cellulase.

-24-

15. Electrically conducting particles comprising an electrically conducting polymer substantially free of coating of a water soluble stabilizing polymer or copolymer of a monomer selected from the group consisting of ethylene oxide, vinyl acetate, vinyl pyrrolidine, carboxymethyl cellulose, vinyl alcohol, and methacrylic acid.

16. The particles of claim 15 wherein the electrically conductive polymer is polymerized from monomers selected from the group consisting of pyrrole, acetylene, aniline, thiophene, and p-phenylene.

17. The particles of claim 15 wherein the polymers are polymerized with an initiator selected from the group consisting of FeCl_3 , FeBr_3 , $\text{Fe}(\text{NO}_3)_3$, $\text{K}_3\text{Fe}(\text{CH})_6$, CuCl_2 , CuBr_2 , $\text{Cu}(\text{NO}_3)_2$, AlCl_3 , BF_3 , SnCl_4 , ZnCl_2 , TiCl_4 , PCl_5 , $\text{RAl}(\text{Cl})_2$, R_2AlCl , R_3Al (wherein R is an organic ion), POCl_3 , CrO_2Cl , SOCl_2 , VOCl_2 , $\text{CH}_3\text{CO}_2\text{ClO}_4$, $\text{K}_2\text{S}_2\text{O}_8$, and $(\text{NH}_4)_2\text{S}_2\text{O}_8$.

18. The particles of claim 15 further comprising a coating of a non-water soluble non-electrically conductive polymer.

19. The particles of claim 15 further comprising a non-electrically conductive latex.

20. The particles of claim 15 further comprising an absorbent.

-25-

21. The particles of claim 15 further comprising material selected from the group consisting of latices, oxides, and carbon.

22. The particles of claim 15 incorporated into a polymeric composite.

23. The particles of claim 15 incorporated into electrodes.

24. The particles of claim 15 further comprising chromatographic or electrophoretic support material.

INTERNATIONAL SEARCH REPORT

International Application No. **PCT/US89/03767**

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC(4): C08F 2/20		
U.S. CL: 526/90		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
U.S.	526/90, 201, 256, 258; 252/500; 524/808	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
<u>X</u> Y	US, A, 4,665,129 (NAARMAN ET AL.) 12 MAY 1987. SEE COLUMN 3, LINES 24-60 AND COLUMN 4, LINES 38-52.	1,3-4,6-8,10, 15-17 1-24
A	US, A, 4,697,000 (WITUCKI ET AL.) 29 SEPTEMBER 1987. SEE THE ENTIRE DOCUMENT.	1-24
Y	EP, A, 0,229,992 (POLAROID CORPORATION) 29 JULY 1987. SEE THE ENTIRE DOCUMENT.	1-24
Y	GB, A, 2,181,367 (ASEA AKTIEBOLAG) 23 APRIL 1987. SEE PAGE 2.	1-24
<u>X</u> Y	JOURNAL OF COLLOID AND INTERFACE SCIENCE, VOLUME 118, NO. 2, ISSUED AUGUST 1987 (ACADEMIC PRESS), BY ARMES, MILLER AND VINCENT, "AQUEOUS DISPERSIONS OF ELECTRICALLY CONDUCTING, MONODISPERSE POLYPYRROLE PARTICLES". SEE THE ENTIRE DOCUMENT.	1-4,6-9,15-19, 21-22 1-24
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
02 NOVEMBER 1989		05 DEC 1989
International Searching Authority		Signature of Authorized Officer
ISA/US		R. H. DELMENDO